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FOR USE OF Fe OXIDE STRIPS TO
DETERMINE ELEMENT BIOAVAILABILITY
IN SOILS

2 Parts

PHOSPHORUS RELEASE FROM SOILS, SPOILS, AND SEDIMENTS:

COMPARISON AMONG DIFFERENT P-SINKS

Report
1 of 2

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PHOSPHORUS RELEASE FROM SOILS, SPOILS, AND SEDIMENTS:

COMPARISON AMONG DIFFERENT P-SINKS

ABSTRACT

Several sinks are currently being used for extraction of P from soils and soil components. A study was conducted to compare and determine the ability of different sinks to remove P from soils, sediments, and spoils in suspension. An anion-exchange resin (AER-HCO₃⁻), anion- plus cation-exchange resin (CAER-H⁺/HCO₃⁻), a mixed-bed resin (MBR-H⁺/OH⁻), an anion-exchange membrane (AEM-HCO₃⁻), and HFO-impregnated filter paper (HFO-strips) were equilibrated for 16 h at a solid:solution ratio of 1:80. Final suspension pH and cation and anions associated with the sinks were determined. Amounts of P released as determined by AER-HCO₃⁻, AEM-HCO₃⁻, HFO-strips, and water extraction (P_w) were closely correlated and, in weakly acidic to calcareous samples, usually limited by Ca²⁺ in solution. In general, dual-resin systems (CAER and MBR) extracted significantly more P than those without a cation-sink. Suspension pH values obtained with AEM-HCO₃⁻ were significantly higher than water paste (1:1) soil pH. Although there were no significant differences in pH between paste soil pH and the other sink systems, CAER-H⁺/HCO₃⁻ produced the lowest suspension pH values. Embedded particles in HFO-strips and probably in AEM may contribute significantly to amounts of P extracted. Although sinks react primarily with the liquid phase, modification of such phase may alter significantly the release from solid phases.

1 Ideally, element bioavailability indices for soils, sediments and
2 natural waters should be obtained through biological methods. Due to cost
3 and time involved in such methods, routine laboratory batch extractions
4 are performed and correlated with existing bioassay data. According to
5 Sibbesen (1983) and Sharpley and Menzel (1987) phosphorus is extracted
6 mainly by : (i) change in pH (acids, bases, and buffers), (ii) introducing
7 anions that will complex/precipitate P- precipitating cations (such as Ca,
8 Al, and Fe), (iii) introducing anions which desorb P and limit its
9 readsorption, (iv) isotopic exchange (^{32}P), and (v) by decreasing the
10 solution P concentration (*mild* extractants and *infinite* sinks).

11 The latter category not only has support from its proponents as the
12 one that resembles more closely biological uptake *in situ* but it is also
13 often used in batch studies of P-release kinetics. *Mild* extractants
14 include distilled and/or deionized water (e.g., Sissingh, 1970; Van der
15 Paauw, 1970; Sharpley *et al.*, 1981), natural waters (e.g., Wang, 1974;
16 Bahnick, 1977), and dilute salt solutions (e.g., Li *et al.* 1972; Barrow,
17 1979). Ion-exchange resins (e.g., Amer *et al.*, 1955; Sibbesen, 1978),
18 ion-exchange membranes (e.g., Saunders, 1964; Cooperband and Logan, 1994),
19 and more recently, Fe-oxide impregnated filter paper (e.g., Van der Zee *et*
20 *al.*, 1987; Menon *et al.* 1989) are P sinks commonly used.

21 *Mild* extractants can closely reproduce field conditions, especially
22 ionic strength and composition of the solution bathing the solid phase.
23 On the other hand, dissolved P is accumulated in solution and readsorption
24 may occur (Munns and Fox, 1976). According to Van der Zee *et al.* (1987),
25 attempts to overcome this problem by extrapolating to "infinite" dilution

and modeling of desorption as a function of time (Barrow, 1979; Barrow et al., 1981; and Sharpley, 1983) are not free from limitations, while the introduction of a sink is a sound alternative approach.

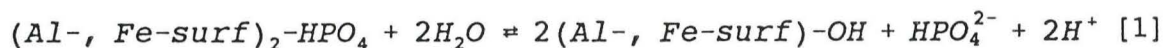
With the exception of some synthetic ion exchangers (chelating and boron specific resins), anion- and cation-exchange resins commonly used are not highly specific and the exchange reactions are fully reversible (BioRad, 1988; Rohm & Haas, 1988). With use of adequate ionic forms and excess exchange capacities, and turning a limitation into an advantage, several multielement resin extraction techniques have been developed (Van Raij et al., 1986; Skogley et al., 1990).

The objective of this study was to compare several sinks and their ability to extract phosphorus from soils, spoils, and sediments. Five different P-sinks were included in this study: (1) an anion-exchange resin (HCO_3^-), (2) anion- plus cation-exchange resin ($\text{H}^+/\text{HCO}_3^-$), (3) a mixed-bed resin (H^+/OH^-), (4) an anion-exchange membrane (HCO_3^-), and (5) a modified HFO-impregnated filter paper technique (Buselli and Amacher, 1994a).

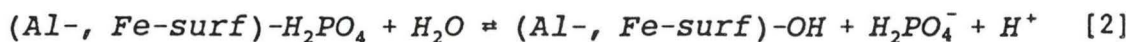
THEORETICAL CONSIDERATIONS

Phosphate release from soils - According to Bache and Ireland (1980), release of P from soils generally involve:

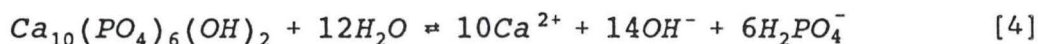
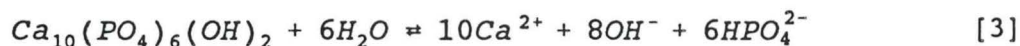
(1) exchange of hydroxyl for phosphate at oxide surfaces:



or



and (2) dissolution of calcium phosphate phases:

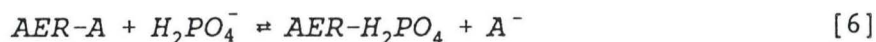


Although there is some debate on the mechanism of chemisorbed phosphate (bidentate versus monodentate) at oxide surfaces (Hingston, et al., 1974; Barrow, 1987), equations [1] through [4] give a simplified, general account of the main products of phosphate release from soils.

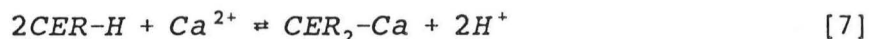
Phosphate uptake by P-sinks - Regardless of the source (desorption or dissolution), phosphate ions are taken up by synthetic anion-exchange materials as both HPO_4^{2-} and $H_2PO_4^-$ (Taylor and Ellis, 1978; Christensen and Posner, 1980),



or



where AER is anion-exchange resin or membrane, and A^- for this set of experiments is either HCO_3^- or OH^- . Similarly, uptake of Ca^{2+} may be expressed as:



where CER is cation-exchange resin. On the other hand, the uptake

mechanism by the HFO-impregnated strips may be represented by the reverse reactions in Eq.[1] and [2].

Dissolution of sparingly soluble solids by ion-exchange resins - According to Helfferich (1962) the amount of resin necessary for complete dissolution of sparingly soluble solids decreases considerably when both anion- and cation-exchange resins are present. Disregarding activity coefficients, electrolyte sorption by the resin, and complex formation, for simplicity, complete dissolution for a 1,1-valent solid is accomplished when:

$$C_C \cdot C_A < K_{SP} \quad [8]$$

where C_C is the cation concentration (mol/L); C_A is the anion concentration (mol/L); and K_{SP} is the solubility product. In the case of CER-H, the amount of resin necessary for complete solid dissolution is given by:

$$\bar{Q} \geq Q_{CA}^0 \left[1 + \frac{(\alpha Q_{CA}^0)^2}{K_{SP} \cdot K_H^C \cdot V^2} \right] \quad [9]$$

where \bar{Q} is the amount of resin (mol_c); Q_{CA}^0 is the amount of solid (mol); α is the degree of dissociation of the acid HA; K_H^C is the selectivity coefficient of the cation; and V is the solution volume (L). When both CER-H and AER-OH are present the amount of exchanger needed is given by:

$$\bar{Q} \geq Q_{CA}^0 \left[1 + \sqrt{\frac{K_W}{K_{SP} \cdot K_H^C \cdot K_{OH}^A}} \right] \quad [10]$$

coefficient of the anion. As a general rule, slightly more than the stoichiometric amounts of resin are needed if

$$K_{SP}^{1/\nu} = K_W^{1/2} \quad [11]$$

where ν is the number of ions into which the solid dissociates (Helfferich, 1962).

MATERIALS AND METHODS

Samples - Table 1 shows the ten soils, representing several Soil Orders, used for this study. Selected soil properties for individual horizons are presented in Table 2. Mine spoils and sediments were collected from an abandoned gold mine in Birch Creek, Nevada (39°23' N 117°05' W, 2190 to 2845 m in elevation) and a phosphate mine in Maybe Canyon, Idaho (42°44' N 111°17' W, 2200 m in elevation). Table 3 shows selected physical and chemical properties for these materials.

Physical and chemical characterization - The soils, sediments, and spoils were air-dried and passed through a 2-mm sieve for particle size analysis. Sand content was determined by wet- and dry-sieving (<53 μ m), clay content in soils was determined by the pipette method and by the hydrometer method in sediments and spoils (Gee and Bauder, 1986); and silt was calculated by difference. Chemical analyses for the soils (Table 2) were conducted by the Soil Testing Laboratory at Louisiana State University on the < 2 mm fraction. Chemical analyses for sediments and spoils (Table 3) were done at the USDA Forestry Sciences Laboratory and at

the Soil Testing Laboratory at Utah State University on the < 0.5 mm fraction. Soil, spoil, and sediment pH was measured using a 1:1 solid/water suspension (McLean, 1982). In soils, total organic carbon (TOC) was determined by wet combustion with gravimetric determination of CO_2 (Nelson and Sommers, 1982) whereas, the dichromate oxidation method with heating was used for spoils and sediments. Soil analysis of carbonate content was conducted by gravimetric determination of CO_2 evolved from treatment with excess H_2SO_4 and FeSO_4 (Nelson, 1982). Determination of calcite and dolomite in sediments and spoils was done by selective dissolution with ammonium acetate at pH 4.5 (Holtzclaw et al., 1986). For the soils (Table 2), cation exchange capacity (CEC) was determined by summing the exchangeable bases plus aluminum as determined by replacement with 0.1 M BaCl_2 - 0.1 M NH_4Cl ; and exchangeable OH^- determined by replacement with F (Perrott et al., 1976). Effective cation exchange capacity (ECEC) for spoils and sediments was determined by replacement with unbuffered 1 M NH_4NO_3 . Free Fe_2O_3 and Al_2O_3 in soils were determined by extraction with dithionite-citrate-bicarbonate (Mehra and Jackson, 1960) following destruction of organic matter using pH 9.5, 5.25% NaOCl (Anderson, 1963); MnO_2 and amorphous Fe_2O_3 were determined by extraction with 0.25 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ - 0.25 M HCl at 50°C (Chao and Zhou, 1983). For sediments and spoils, crystalline Fe was determined by the ascorbic acid - oxalate method of Shuman (1982), MnO_2 with hydroxylamine hydrochloride at pH 2.0 (Chao, 1972), and amorphous Fe with hydroxylamine hydrochloride - hydrochloric acid (Chao and Zhou, 1983).

Water and Sequential (Base - Acid) Extraction - Water extractions (Pw)

were carried out by placing 2.0 g of air dried material (soil, spoil, or sediment) in 50-ml centrifuge tubes and adding 20-ml of deionized water (di-water). Samples were shaken for 24 h in a reciprocating shaker at 120 rpm. The tubes were centrifuged for 10 min at 1500 g and the supernatant filtered through a 0.4 μ m Micropore filter. For the sequential extractions, 0.5 g of air dried material was placed in a 50-ml plastic centrifuge tube and 25-ml of 0.1 M NaOH - 0.1 M NaCl added. The tubes were shaken for 24 h at 120 rpm in a reciprocating shaker and centrifuged for 10 min at 1500 g. The supernatant was collected for analysis. The samples were washed three times with 95% ethanol, and air dried. Twenty five ml of 1 M HCl were added, and the tubes were shaken for another 24 h. The samples were centrifuged, and the supernatant saved for analysis. Analyses were carried by ICAPES, and any samples below 2 mg P/L were also analyzed colorimetrically (Murphy and Riley, 1962)

HFO-impregnated strips - All experiments involving a P-sink were carried out in duplicate. Preparation of the modified HFO-impregnated strips was done according to the method of Buselli and Amacher (1994a). Experiments were carried out using 1.00 g of air dried material ($< 250 \mu$ m) in 80 ml of 0.01 M CaCl_2 and shaken in an orbital shaker for 16 h at 150 rpm and $25 \pm 1^\circ\text{C}$. Then, the strips were removed and washed thoroughly, dismounted from the plastic frames, washed again in di-water and placed in 50-ml plastic centrifuge tubes. Extractions were done in a reciprocating shaker at 180 rpm using 25 ml of 0.25 N $\text{NH}_2\text{OH}\cdot\text{HCl}$ + 0.25 N HCl for 15 min. Extracted solutions were analyzed by ICAPES. According to previous findings (Buselli and Amacher, 1994c), duplicate filter paper blanks were included

in all HFO-strip extractions.

Ion-exchange resins - Ion-exchange resin beads were sieved before use and the $> 500 \mu\text{m}$ size fraction collected and rinsed thoroughly. Two mmol_c of anion- or cation-exchange resins or 4 mmol_c of mixed-bed resin (MBR) were placed in polyethylene bags (3x6 cm, Spectra/Mesh®, mesh opening $292 \mu\text{m}$) sealed and converted to the desired form. For the anion-exchange resin (AER) and the MBR experiments one bag and 1.00 g of air dried material were suspended in 80 ml of di-water. For the cation- plus anion-exchange resin (CAER) experiments one bag of each resin (cation and anion) was suspended with 1.00 g of air-dried material in 80 ml di-water. Table 4 shows the characteristics of the different resin sinks used in this study. All extractions were carried out in 250-ml polycarbonate jars, and the suspensions were shaken at 150 rpm in an orbital shaker at 25°C . After shaking for 16 h the resin-bags were removed, washed thoroughly, placed in 40 ml of 1 N HCl and eluted for 1 h. Then the bags were removed and the eluant analyzed by ICAPES.

Ion-exchange membrane - Squares (6cm x 6cm) of Ionics AR.204, an acrylic fiber-backed membrane (Ionics, Inc., Watertown, MA), were cut and treated with 2 N HCl twice, for one hour, to remove impurities. Subsequently, they were converted to the HCO_3^- -form. One anion-exchange membrane (AEM) square ($\sim 2 \text{mmol}_c$) was placed with 1.00 g of air dried material in 80 ml di-water following the same extraction procedure as with the ion-exchange resins.

Regeneration of ion-exchange materials - Except for the MBR-bags, which were prepared with fresh resin before use, all other ion-exchange

materials were regenerated and reused. Anion-exchange materials (AER and AEM) were regenerated with 0.5 N NaHCO_3 and cation-exchange resins with 0.5 N HCl. Eight bags or squares were placed in a 250-ml jar and 200 ml of the regenerating solution added. The jars were shaken for an hour and rinsed thoroughly with distilled water. The procedure was repeated two more times with regenerating solution followed by three more times with di-water.

RESULTS AND DISCUSSION

Phosphorus extracted by water (Pw) and by different P-sinks is shown in Figure 1. Sink systems containing both anion- and cation-exchange resins extracted larger amounts of P, especially from sediments and spoils. Amounts of P extracted from soils by Pw, HFO-Strip, HFO-Strip Corrected, AER- HCO_3^- , and AEM- HCO_3^- were very highly correlated ($P < 0.001$), but this was not the case for amounts extracted from sediments and spoils (Table 5). Data presented by Lin et al. (1991) also show very highly significant coefficients of correlation among P extracted by water, HFO-strips, and AER- HCO_3^- for 39 soils from Taiwan.

Data for the HFO-impregnated filter paper technique, shown in Table 6, includes filter paper blanks (F-Blk), actual P removed from suspension by the strips (HFO-Strip), and values calculated by subtraction F-Blks from HFO-Strips (HFO-Strip Corr.). For the 13 soils, correction for blanks slightly improved the correlation between the technique and Pw, and made no difference when correlated with AER or AEM (Table 5). On the

other hand, blank correction lowered the r values for correlations with all resin systems for sediments and spoils as well as overall ($n = 18$) correlations. Similar reductions in r values between Olsen-P and HFO-strip-P, after correcting for embedded particles, have been found by Perrot and Wise (1993) with phosphate rock treated soils from New Zealand. Although numerous reports in which significant correlations between plant P uptake (e.g., Menon et al. 1991a; 1991b), as well as yield (Kumar et al., 1992), and P test values obtained with the iron oxide-impregnated filter paper technique have been recently published, caution is recommended when interpreting the results. This is especially true with soils fertilized with sparingly soluble P-sources (e.g., rock phosphate). Detailed descriptions of the effects of embedded particles on HFO-strip-P can be found elsewhere (Perrott and Wise, 1993; Buselli and Amacher, 1994c).

The influence of calcium removal on P release from soils is well documented for both desorption of adsorbed P (e.g., Smillie, et al., 1987) and for dissolution of particulate Ca phosphates (e.g., Robinson, et al., 1992). According to Curtin et al. (1987), release of adsorbed P is enhanced by the removal of exchangeable divalent cations (i.e., Ca and Mg) which, in turn, increases surface negative potential, thus favoring P desorption. Working with 11 acid soils (pH_{H_2O} 1:1, 5.0 to 6.3) from New Zealand, they found a strong correlation ($r = 0.99^{**}$) between P extracted by AER- HCO_3 and that removed by sequential water extraction. On the other hand, pretreatment of soils with 1 M NaCl not only increased the amounts of P extracted by sequential water extraction, but were in close

correlation with P values extracted by AER-OH + CER-H. Their results suggest that, even in acid soils, exchangeable Ca (or Mg) influences P desorption and that, by replacing divalent cations from the exchange complex or introducing a divalent cation-sink, increased P desorption is likely. From equations [3] and [4] and applying solubility-product principles, the effect of Ca^{2+} removal from solution on the dissolution of Ca-phosphate phases can be easily predicted. In soils, according to Robinson et al. (1992), leaching is an important sink for Ca^{2+} . Although phosphate and hydroxyl ions are not easily leached from soils, release of soil-supplied protons may provide a sink for OH^- . In batch studies, removal of Ca^{2+} from solution can be accomplished by precipitation of Ca products (e.g., CaCO_3) or by the introduction of a Ca-sink.

Our phosphorus release data, for the most part (Fig. 1 and Tables 6 & 7), is in agreement with the findings of Syers and co-workers (Curtin et al., 1987; Smillie et al., 1987; Robinson et al., 1992). Even with relatively acid soils (e.g., Alligator, $\text{pH}_{\text{H}_2\text{O}}$ 1:1, 4.8) introduction of a Ca-sink results in a significant increase in P release. This increase being more significant with materials high in calcium (e.g., MC phosphate mine spoils, Calciorthid and Webster soils). For the soils, introduction of cation-exchange resin, as compared to AER alone, resulted in increased P release except in soils containing significant amounts of short-range-ordered or "amorphous" oxides (i.e., Andepts and Oxisol). In those soils, small variations in suspension pH may significantly influence P release (see Eqs. [1] and [2]). For sediments and spoils, presence of CER resulted in significant increases in P release for the Maybe Canyon

materials. Except for the Gray Mine Spoil, slight increases in P
extraction occurred with the materials collected from Birch Creek. In the
BC samples large amounts of sulfate were extracted by the four resin-sink
systems. Average S-extraction values ($n = 8$) were 164.9 (SE 9.1) mmol
S/kg for the Sediment Basin sample, 21.7 (SE 1.4) for the Gray Mine Spoil
and 69.8 (SE 2.0) mmol S/kg for the Black Mine Spoil. The closeness of
the S values extracted by the four systems, suggests that, presence of a
Ca-sink had little or no influence on the S uptake by anion-exchange
materials even when considerable amounts of calcium have been removed
(Table 7).

Eventhough closely correlated, AEM-HCO₃ extracted larger amounts of
P than AER-HCO₃. It is important to note that, both AER and AEM removed
Ca from suspension, probably through adhering particles. Amounts of Ca
extracted from AER bags were no higher than 0.28 mmol Ca/kg of material,
whereas those extracted from AEM were up to 3.39 mmol Ca/kg. Also, use of
AEM-HCO₃ produced the highest suspension pH values (Fig. 2).

Regardless of individual limitations of each technique, we can
assume that, a single water extraction (Pw), HFO-Strips, AER-HCO₃, and AEM-
HCO₃, extract, in general, the same fraction of soil-P and that, in soils
with high exchangeable Ca and/or Ca solid phases, dissolved Ca²⁺ limits
further P release. Improvement in correlations between plant P-uptake and
P extracted by sinks has been widely reported when soils are partitioned
into calcareous or non calcareous (e.g., Sharpley, 1991; Tran et al.,
1992). In calcareous soils, build up of Ca²⁺ in solution may be partly
responsible for the improvement in r values when such partitioning is

used.

If P release includes significant amounts of solid phase dissolution, CER + AER systems outperform single resin ones. Using the simplified equations [9] and [10], Helfferich (1962) calculated the amounts needed for dissolution of AgCl using CER-H versus CER-H + AER-OH. For complete dissolution, from 300 to 600 times more single (CER or AER) resin, by weight, is needed than in mixed CER + AER systems. Another factor to consider is the dependence of single resin on solution volume, which may be considered as "storage" for the co-ion, per unit volume, up to IAP equal K_{sp} (Eq. [9]). Thus, mixed-bed resins (especially in H^+/OH^- form) are less dependent on soil:solution ratios than single resin systems. Some concerns have been expressed about the reactivity of H^+/OH^- charged resins toward crystalline soil components and "non-plant-available" forms (e.g., Frenkel et al., 1986; Tran et al., 1992). While this has been observed for CER-H (e.g., French et al., 1984) and AER-OH (e.g., Sibbesen, 1978) single-resin systems, our data and that of others (Curtin et al., 1987), suggest that in combined H^+/OH^- charged systems this is not the case. Curtin et al. (1987) found a close correlation between P extracted with NaCl followed by sequential water extractions. Furthermore, total amounts extracted were quite similar, indicating similarity in the release mechanisms. Suspension pH values from our data (Fig. 2) suggest no significant changes when compared to pH_{H_2O} 1:1 values. Apparently, due to high H^+ mobility, in well stirred suspensions there are no significant localized reactions. Similar amounts of Al, Si, K, and Fe were extracted (data not shown) by both dual-resin systems (CAER and MBR),

indicating that, even when resins are physically separated in individual bags, as compared to single bag-MBR, localized reactions are not significant.

Studies with resin systems containing both CER + AER have been carried out mostly with resins in Na^+/Cl^- (e.g., Vaidyanathan and Talibudeen, 1970; Dalal, 1985), $\text{NH}_4^+/\text{Cl}^-$ (Peaslee, 1969), $\text{Na}^+/\text{HCO}_3^-$ (e.g., Van Raij et al., 1986; Saggar et al., 1990), Na^+/OH^- (Curtin et al., 1987), $\text{H}^+/\text{HCO}_3^-$ (this study), H^+/OH^- (e.g., Curtin et al., 1987; Tran et al., 1992), and H^+/Cl^- form (Skogley et al., 1990). In general, dual-resin systems have been found to extract more P than AER alone, even though some of the comparisons have been done using the same weight or volume of single- and dual-resins, which results in dual-resins having approximately half as much anion-exchange capacity (e.g., Dalal, 1985; Tran et al., 1992). Besides resin capacity, which is more critical in single-resin systems, ion-exchange selectivities are usually disregarded. Table 8 shows typical relative selectivities for strong-acid and strong-base exchange resins. Whereas differences in relative selectivities between cations usually present in soil solutions are not large, relative selectivities of anions can be considerably different. Another important observation that can be derived from Table 8 is that, anions loosely held by soils (e.g., Cl^- , NO_3^-) are generally preferred by the resins over more strongly held anions (e.g., HPO_4^{2-} , F^-). Therefore, of the three forms of AER commonly used in dual-resin P-extractions, OH^- is easily replaced by other anions, whereas Cl^- is more strongly held. Additionally, as pointed out by Bache and Ireland (1980), HCO_3^- may hydrolyse in two different ways,

may precipitate as CaCO_3 , or may be directly adsorbed to (oxy)hydroxide surfaces. Hydroxyls may replace adsorbed anions from soil surfaces, or combine with H^+ to form water. On the other hand, Cl^- ions, apart of certain degree of complexation in solution, are not strongly held by soil surfaces and any Cl^- present in the soil plus the amounts released by the AER will remain in solution. Therefore, not only ionic strength will increase but Cl^- in solution, being preferred by the resin over HPO_4^{2-} and H_2PO_4^- (Christensen and Posner, 1980; also Table 8), will displace phosphate already sorbed by the AER.

Changes in suspension pH caused by the introduction of exchangers, as seen from equations [1] through [4], will affect P release significantly. Although difficult to predict *a priori*, especially with dual-resin systems, some general idea of the direction in pH change can be deduced from the ionic form(s) of the ion-exchange resins. Curtin et al. (1987), attributed the failure of dual-resin in Na^+/OH^- form to dissolve Ca phosphate phases to suspension alkalinity (pH 8.7). Saggar et al. (1992) reported suspension pH values of dual-resin-membranes in $\text{Na}^+/\text{HCO}_3^-$ from ~6 to 8, whereas for AEM- HCO_3^- were ~6.2. Skogley et al. (1990), found increased P-release and lower removal of K and S when using dual-resin in H^+/OH^- as compared to H^+/Cl^- for 20 Montana soils, but no suspension pH values were reported. Our resin suspension pH values (Fig. 2), show no significant differences in pH values between $\text{pH}_{\text{H}_2\text{O}}$ 1:1 and H^+/OH^- form MBR. CAER in $\text{H}^+/\text{HCO}_3^-$ form produced slightly lower suspension pH values, but the difference was not significant even at the 5% level. On the other hand, overall suspension pH values obtained with AEM- HCO_3^- were significantly

($P < 0.05$) higher than all other resin systems and paste soil pH. Even though changes in pH from introduction of sinks occurs, extractions can be considered relatively mild, and no significant correlations were found between the different methods and P extracted by either NaOH and/or HCl (sequential extractions, Table 6).

CONCLUSIONS

Although P-sinks, such as HFO-Strips and resins, are considered to react with the liquid phase of the suspension and not with soil components (Perrot et al., 1993), their interaction and modification of the liquid phase has considerable effects on the uptake/release characteristics of the soils. Unlike standard extraction procedures (Olsen's-P, Bray, etc.), where a solid and a liquid phase are allowed to equilibrate, introduction of a sink adds a third phase. Therefore, not only does solid:solution ratio, temperature, shaking speed, and container shape influence the extraction, but also the characteristics and size of the sink. Preparation of the HFO-strips, as well as resin functional groups, degree of DVB cross-linkage, particle size, ionic-form(s), exchange capacity, and type of bag (if any), affect the solid:solution:sink equilibrium.

Build up of Ca^{2+} in solution, in weakly acidic to calcareous soils, both from exchangeable and dissolved solid phase sources, limits the release of P. Introduction of an effective Ca-sink maintains the levels in solution low as to allow continued release. The Ca-sink characteristics of HFO-strips are not significant at pH values below 8

(Buselli and Amacher, 1994a; 1994b) and HFO-strip P correlates with amounts extracted by both AER-HCO₃ and AEM-HCO₃. Therefore, extraction of P after a certain point becomes dependent on Ca²⁺ in solution and not on the fraction of P easily released.

The advantages of using AER in HCO₃⁻ form over Cl⁻, not only stem from the fact that HCO₃⁻ is not conserved in solution (Bache and Ireland, 1980) but also from their relative selectivities. Furthermore, by not being conserved, HCO₃⁻ release does not increase the ionic strength of the solution and readsorption of HCO₃⁻ by the resin is reduced. Introduction of dual-resin systems in the H⁺/OH⁻ form, has the advantage of (1) providing a sink for cations (e.g., calcium), (2) counterions are not conserved in solution, and (3) there are no significant changes in suspension pH values. Even dual-resin systems in H⁺/HCO₃⁻ form only showed a slight decrease in suspension pH.

The effect of embedded particles on AEM, as well relatively large increase in suspension pH, as compared to AER, should be studied further. Rigid sinks (HFO-strips and AEM) have the advantage of being easy to use and can be separated from suspension almost instantaneously. On the other hand, suspended particles can adhere to HFO-strips (Buselli and Amacher, 1994c) and apparently also to AEM.

Complete analysis of extractant solutions, used to remove sorbed species from sinks, should be obtained. Valuable information about embedded particles as well as competition of other species present can be gained. Due to the non-specificity of the sinks towards major ions in soil solutions, presence of other ions can influence the removal of the

ion of interest (e.g., SO_4^{2+} on PO_4^{3-} , this study; Cooperband and Logan, 1994).

Eventhough some of these concepts have been known for quite some time, the use of single-resin sinks, usually in the chloride form still prevails in the literature. Recently, dual-resin capsules in the H^+/OH^- form have been made commercially available (UNIBEST Inc., Bozeman, MT), based on the studies of Skogley and co-workers (Skogley et al., 1990). Further studies with dual-resin systems using pure soil components and soils can greatly help our understanding of the chemistry of element release as well as interactions between release of different elements.

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Table 1. Taxonomic classification and origin of samples

| Soil | Taxonomic classification | State |
|-----------|---|----------------|
| Alligator | Vertic Haplaquept, very-fine, montmorillonitic, acid, thermic | Louisiana |
| Unnamed | Calciorthid | New Mexico |
| Cecil | Typic Hapludult, clayey, kaolinitic, thermic | South Carolina |
| Kula | Typic Euthandept, medial, isothermic | Hawaii |
| Lafitte | Typic Medisaprist, euic, thermic | Louisiana |
| Molokai | Typic Torrox, clayey, kaolinitic, isohyperthermic | Hawaii |
| Norwood | Typic Udifluvent, fine-silty, mixed, calcareous, thermic | Louisiana |
| Olivier | Aquic Fragiudalf, fine-silty, mixed, thermic | Louisiana |
| Webster | Typic Haplaquoll, fine-loamy, mixed, mesic | Iowa |
| Windsor | Typic Udipsamment, mixed, mesic | New Hampshire |

Table 2. Selected soil properties for some soil samples studied (< 2 mm size fraction).

| Soil | Horizon | pH | TOC ^a % | CEC ^b cmol _c /kg | OH ^c | MnO ₂ % | % Fe ₂ O ₃ | | Al ₂ O ₃ | CaCO ₃ | Sand % | Silt | Clay |
|-----------|---------|-----|-----------------------|---|-----------------|-----------------------|----------------------------------|-------|--------------------------------|-------------------|-----------|------|------|
| | | | | | | | Amor. | Free. | | | | | |
| Alligator | Ap | 4.8 | 1.54 | 30.2 | 3.5 | 0.028 | 0.33 | 0.74 | 0.15 | - | 5.9 | 39.4 | 54.7 |
| Unnamed | Ap | 8.5 | 0.44 | 14.7 | 33.8 | 0.015 | 0.050 | 0.25 | 0.000 | 7.39 | 70.0 | 19.3 | 10.7 |
| Cecil | Ap | 5.7 | 0.61 | 2.0 | 2.0 | 0.011 | 0.099 | 1.76 | 0.27 | - | 78.8 | 12.9 | 8.3 |
| Cecil | B | 5.4 | 0.26 | 2.4 | 6.6 | 0.002 | 0.082 | 7.48 | 0.94 | - | 30.0 | 18.8 | 51.2 |
| Kula | Ap1 | 5.9 | 6.62 | 22.5 | 82.4 | 0.093 | 1.68 | 5.85 | 3.51 | - | 73.7 | 25.4 | 0.9 |
| Kula | Ap2 | 6.2 | 6.98 | 27.0 | 58.5 | 0.13 | 1.64 | 6.95 | 3.67 | - | 66.6 | 32.9 | 0.5 |
| Lafitte | Ap | 3.9 | 11.6 | 26.9 | 4.7 | 0.009 | 1.19 | 1.16 | 0.28 | - | 60.7 | 21.7 | 17.6 |
| Molokai | Ap | 6.0 | 1.67 | 11.0 | 7.2 | 0.76 | 0.19 | 12.4 | 0.91 | - | 25.7 | 46.2 | 28.2 |
| Norwood | Ap | 6.9 | 0.21 | 4.1 | 0.0 | 0.008 | 0.061 | 0.30 | 0.016 | - | 79.2 | 18.1 | 2.8 |
| Olivier | Ap | 6.6 | 0.83 | 8.6 | 1.9 | 0.27 | 0.30 | 0.71 | 0.071 | - | 4.4 | 89.4 | 6.2 |
| Webster | Ap | 7.6 | 4.39 | 48.1 | 14.1 | 0.063 | 0.19 | 0.55 | 0.10 | 3.14 | 27.5 | 48.6 | 23.9 |
| Windsor | Ap | 5.3 | 2.03 | 2.0 | 10.2 | 0.041 | 0.42 | 1.23 | 0.56 | - | 76.8 | 20.5 | 2.8 |
| Windsor | B | 5.8 | 0.67 | 0.8 | 10.1 | 0.031 | 0.23 | 0.79 | 0.29 | - | 74.8 | 24.1 | 1.1 |

^a TOC - Total organic carbon^b CEC - Cation exchange capacity^c OH - Exchangeable hydroxyl

Table 3. Selected properties for sediment and mine spoil samples studied. Chemical characterization done on the < 0.5 mm size fraction, particle size analysis on the < 2.0 mm size fraction.

| Sample | Mine ^a | pH | TOC ^b | ECEC ^c | MnO ₂ | % Fe ₂ O ₃ | | % Carbonates | | Sand | Silt | Clay |
|---------------------|-------------------|-------------------|------------------|-----------------------|------------------|----------------------------------|--------------------|-------------------|-------------------|------|------|------|
| | | | % | cmol _c /kg | % | Amor. ^d | Crys. ^e | Dol. ^f | Cal. ^g | | | |
| Mine Sediment Basin | BC | 6.9 | 1.54 | 47.86 | 0.051 | 1.652 | 1.108 | 0.29 | 2.57 | 29.1 | 42.9 | 28.1 |
| Gray Mine Spoil | BC | 7.5 | 1.09 | 19.83 | 0.043 | 1.711 | 0.258 | 0.50 | 2.86 | - | - | - |
| Black Mine Spoil | BC | 3.2 | 3.06 | 6.64 | 0.016 | 1.557 | 0.281 | 0.00 | 0.00 | - | - | - |
| Mudstone | MC | 7.5 | 5.25 | 24.77 | 0.031 | 0.649 | 1.103 | 0.15 | 0.36 | 37.5 | 43.5 | 19.0 |
| Chert | MC | 6.3 | 0.76 | 3.76 | 0.125 | 0.112 | 0.657 | 0.00 | 0.08 | 66.9 | 23.4 | 9.7 |
| Sediment #1 | MC | 7.39 ^h | 2.80 | 26.40 | 0.365 | 0.723 | 1.025 | 0.04 | 0.15 | 48.1 | 33.8 | 18.1 |
| Sediment #2 | MC | 8.29 ^h | 1.43 | 16.01 | 0.145 | 0.557 | 0.599 | 0.06 | 0.10 | 57.6 | 34.2 | 8.2 |

^a Mines: BC, Birch Creek, NV; MC, Maybe Canyon, ID.

^b TOC - Total organic carbon

^c ECEC - Effective cation exchange capacity

^d Amor. - Amorphous

^e Crys. - Crystalline

^f Dol. - Dolomite

^g Cal. - Calcite

^h pH of overlying water

Table 4. Properties of the different ion-exchange materials.

| Sink | Type | Product | % DVB ^a | Capacity ^b mol _c /kg | Form |
|------|--------------------------------|---|--------------------|---|---------------------------------|
| AER | Anion-exchange resin | Amberlite IR-120Plus | 8 | 3.8 | HCO ₃ ⁻ |
| MBR | Cation- & anion-exchange resin | Amberlite MB1 (mixed-bed) ^c | 8 | ~4.1 | H ⁺ /OH ⁻ |
| CAER | Cation- & anion-exchange resin | Amberlite IRA-400 & | 8 | 4.4 | H ⁺ |
| | | Amberlite IR-120Plus | 8 | 3.8 | HCO ₃ ⁻ |
| AEM | Anion-exchange membrane | Ionics AR-204 | - | 0.5425 ^d | HCO ₃ ⁻ |

^a % DVB - % crosslinkage with divinylbenzene

^b Capacity on a dry weight basis, except ion-exchange membrane

^c Mixed-bed ion-exchange resin is a physical mixture of Amberlite IRA-400 & Amberlite IRA-120

^d Membrane capacity expressed in mol_c/m²

Table 5. Coefficients of correlation (r) among the different P-extractants.

| X | Y | Soils (n = 13) | Sediments & Spoils (n = 7) | Total (n = 18) |
|---|---|-------------------|-------------------------------|-------------------|
| Pw | Filter Blank | 0.08 | 0.52 | 0.56* |
| | HFO-Strip | 0.93*** | 0.66 | 0.73*** |
| | HFO-Strip Corrected | 0.94*** | 0.67 | 0.62** |
| | AER (HCO ₃ ⁻) | 0.93*** | 0.86* | 0.87*** |
| | CAER (HCO ₃ ⁻ /H ⁺) | 0.72** | 0.30 | 0.39* |
| | MBR (OH ⁻ /H ⁺) | 0.60* | 0.27 | 0.37 |
| | AEM (HCO ₃ ⁻) | 0.95*** | 0.63 | 0.72*** |
| Filter Blank | HFO-Strip | 0.03 | 0.98*** | 0.92*** |
| | HFO-Strip Corrected | 0.04 | 0.12 | 0.13 |
| | AER (HCO ₃ ⁻) | 0.05 | 0.73 | 0.70*** |
| | CAER (HCO ₃ ⁻ /H ⁺) | 0.30 | 0.97*** | 0.97*** |
| | MBR (OH ⁻ /H ⁺) | 0.27 | 0.95*** | 0.96*** |
| | AEM (HCO ₃ ⁻) | 0.04 | 0.87* | 0.79*** |
| HFO-Strip | HFO-Strip Corrected | 1.00*** | 0.08 | 0.50* |
| | AER (HCO ₃ ⁻) | 0.91*** | 0.84* | 0.87*** |
| | CAER (HCO ₃ ⁻ /H ⁺) | 0.74** | 0.91** | 0.87*** |
| | MBR (OH ⁻ /H ⁺) | 0.63* | 0.89** | 0.87*** |
| | AEM (HCO ₃ ⁻) | 0.93*** | 0.93** | 0.94*** |
| HFO-Strip Corrected | AER (HCO ₃ ⁻) | 0.91*** | 0.52 | 0.69*** |
| | CAER (HCO ₃ ⁻ /H ⁺) | 0.72** | 0.34 | 0.06 |
| | MBR (OH ⁻ /H ⁺) | 0.61* | 0.33 | 0.07 |
| | AEM (HCO ₃ ⁻) | 0.93*** | 0.25 | 0.65** |
| AER (HCO ₃ ⁻) | CAER (HCO ₃ ⁻ /H ⁺) | 0.73** | 0.58 | 0.60** |
| | MBR (OH ⁻ /H ⁺) | 0.61* | 0.59 | 0.61** |
| | AEM (HCO ₃ ⁻) | 0.99*** | 0.92** | 0.95*** |
| CAER (HCO ₃ ⁻ /H ⁺) | MBR (OH ⁻ /H ⁺) | 0.97*** | 0.99*** | 0.99*** |
| | AEM (HCO ₃ ⁻) | 0.70** | 0.80* | 0.74*** |
| MBR (OH ⁻ /H ⁺) | AEM (HCO ₃ ⁻) | 0.57* | 0.82* | 0.76*** |

* Significant at P = .05

** Significant at P = .01

*** Significant at P = .001

Table 6. Amounts of P in mmol P/kg of material obtained with several extraction procedures

| | Sequential Extr. | | Pw | F-Blk | HFO-Strip | HFO-Corr |
|------------------------|------------------|--------|------|-------|-----------|----------|
| | NaOH | HCl | | | | |
| Alligator Ap | 4.52 | 8.72 | 0.20 | 0.05 | 1.78 | 1.72 |
| Calciorthid | 0.05 | 7.91 | 0.02 | 0.13 | 0.29 | 0.17 |
| Cecil Ap | 1.71 | 0.11 | 0.01 | 0.02 | 0.10 | 0.08 |
| Cecil B | 4.84 | 0.03 | 0.00 | 0.02 | 0.03 | 0.01 |
| Kula Ap1 | 61.67 | 23.89 | 0.02 | 0.08 | 0.15 | 0.07 |
| Kula Ap2 | 64.09 | 18.56 | 0.01 | 0.08 | 0.12 | 0.04 |
| Laffitte Muck | 13.72 | 3.23 | 0.02 | 0.02 | 0.20 | 0.17 |
| Molokai Ap | 17.76 | 0.69 | 0.13 | 0.04 | 0.57 | 0.54 |
| Norwood | 0.10 | 10.01 | 0.02 | 0.05 | 0.22 | 0.17 |
| Olivier | 1.63 | 1.66 | 0.03 | 0.03 | 0.31 | 0.29 |
| Webster | 0.06 | 8.23 | 0.08 | 0.04 | 0.47 | 0.43 |
| Windsor A | 19.37 | 3.71 | 0.02 | 0.05 | 0.13 | 0.08 |
| Windsor B | 11.78 | 5.33 | 0.01 | 0.05 | 0.12 | 0.06 |
| Mine Sediment Basin BC | 4.28 | 47.46 | 0.00 | 0.00 | 0.32 | 0.32 |
| Gray Mine Spoil BC | 1.16 | 32.29 | 0.04 | 0.00 | 0.61 | 0.61 |
| Black Mine Spoil BC | 82.49 | 36.48 | 0.03 | 0.08 | 0.57 | 0.48 |
| Mudstone MC | 0.74 | 952.44 | 0.12 | 3.79 | 4.00 | 0.20 |
| Chert MC | 6.78 | 213.09 | 0.59 | 2.30 | 3.35 | 1.05 |
| Sediment #1 MC | 1.31 | 148.68 | 0.06 | 0.36 | 1.05 | 0.69 |
| Sediment #2 MC | 1.40 | 258.94 | 0.09 | 0.52 | 1.37 | 0.85 |

Table 7. Amounts of Ca and P released from different materials to resin-sink systems.

| | mmol P/kg of material | | | | mmol Ca/kg of material | | | |
|------------------------|-----------------------|--------|--------|------|------------------------|--------|--------|------|
| | AER | CAER | MBR | AEM | AER | CAER | MBR | AEM |
| Alligator Ap | 1.94 | 4.07 | 3.81 | 2.97 | 0.01 | 6.79 | 5.42 | 0.07 |
| Calciorthid | 0.59 | 3.36 | 3.44 | 0.75 | 0.28 | 205.24 | 253.09 | 0.67 |
| Cecil Ap | 0.05 | 0.12 | 0.10 | 0.16 | 0.00 | 1.29 | 0.72 | 0.00 |
| Cecil B | 0.04 | 0.26 | 0.24 | 0.03 | 0.05 | 2.68 | 2.00 | 0.00 |
| Kula Ap1 | 0.25 | 0.46 | 0.30 | 0.52 | 0.02 | 18.76 | 11.93 | 0.08 |
| Kula Ap2 | 0.40 | 0.35 | 0.36 | 0.53 | 0.03 | 20.14 | 21.71 | 0.24 |
| Laffitte Muck | 0.70 | 1.00 | 1.43 | 0.94 | 0.00 | 18.80 | 15.77 | 0.08 |
| Molokai Ap | 1.31 | 1.90 | 1.21 | 1.93 | 0.01 | 11.95 | 3.41 | 0.03 |
| Norwood | 0.27 | 1.39 | 1.32 | 0.43 | 0.01 | 38.55 | 43.61 | 0.17 |
| Olivier | 0.51 | 1.08 | 0.85 | 0.68 | 0.00 | 10.58 | 3.81 | 0.06 |
| Webster | 0.62 | 3.75 | 4.65 | 0.81 | 0.07 | 118.42 | 131.97 | 0.46 |
| Windsor A | 0.26 | 0.28 | 0.46 | 0.27 | 0.00 | 9.43 | 3.23 | 0.01 |
| Windsor B | 0.05 | 0.13 | 0.28 | 0.19 | 0.00 | 6.46 | 0.97 | 0.06 |
| Mine Sediment Basin BC | 0.11 | 0.19 | 0.12 | 0.10 | 0.10 | 191.35 | 107.28 | 0.86 |
| Gray Mine Spoil BC | 0.70 | 0.52 | 0.43 | 1.43 | 0.03 | 94.08 | 61.72 | 0.49 |
| Black Mine Spoil BC | 0.10 | 1.02 | 1.25 | 0.79 | 0.00 | 18.00 | 0.59 | 0.09 |
| Mudstone MC | 2.12 | 152.65 | 138.96 | 4.39 | 0.20 | 219.36 | 137.20 | 3.39 |
| Chert MC | 3.42 | 53.34 | 46.10 | 4.00 | 0.08 | 51.50 | 20.22 | 0.68 |
| Sediment #1 MC | 1.74 | 14.92 | 28.48 | 2.74 | 0.02 | 52.92 | 37.21 | 0.65 |
| Sediment #2 MC | 1.20 | 8.14 | 11.04 | 2.16 | 0.01 | 37.51 | 19.37 | 0.57 |

Table 8. Relative selectivity of various counterions on strongly acid and strongly basic ion-exchange resins (Biorad, 1994).

| Counterion | CER ¹ | Counterion | AER ² |
|------------------------------|------------------|---|------------------|
| H ⁺ | 1.0 | OH ⁻ | 1.0 |
| Na ⁺ | 1.5 | F ⁻ | 1.6 |
| NH ₄ ⁺ | 1.95 | H ₂ PO ₄ ⁻ | 5.0 |
| Mn ²⁺ | 2.35 | IO ₃ ⁻ | 5.5 |
| K ⁺ | 2.5 | HCO ₃ ⁻ | 6.0 |
| Mg ²⁺ | 2.5 | Cl ⁻ | 22 |
| Zn ²⁺ | 2.7 | NO ₂ ⁻ | 24 |
| Cu ²⁺ | 2.9 | Br ⁻ | 50 |
| Cd ²⁺ | 2.95 | NO ₃ ⁻ | 65 |
| Ni ²⁺ | 3.0 | HSO ₄ ⁻ | 85 |
| Ca ²⁺ | 3.9 | I ⁻ | 175 |

¹ Biorad AG 50W-X8 resin

² Biorad AG 1-X8 resin

FIGURES

Figure 1. Average P extraction by different methods for soils ($n = 13$) and sediments and spoils ($n = 7$). Pw, water extraction 1:1; F, filter paper blanks; HFO, HFO-strips; HFO-Corr, HFO-strips after correcting for blanks; AER, anion-exchange resin in HCO_3^- -form; CAER, cation-exchange resin in H^+ -form + AER in HCO_3^- -form; MBR, mixed-bed resin in H^+/OH^- -form; AEM, anion-exchange membrane in HCO_3^- -form.

Figure 2. Average suspension pH values for the four resin systems, 1:1 refers to pH measured in water:soil pastes.

Figure 1

mmol P / kg of material

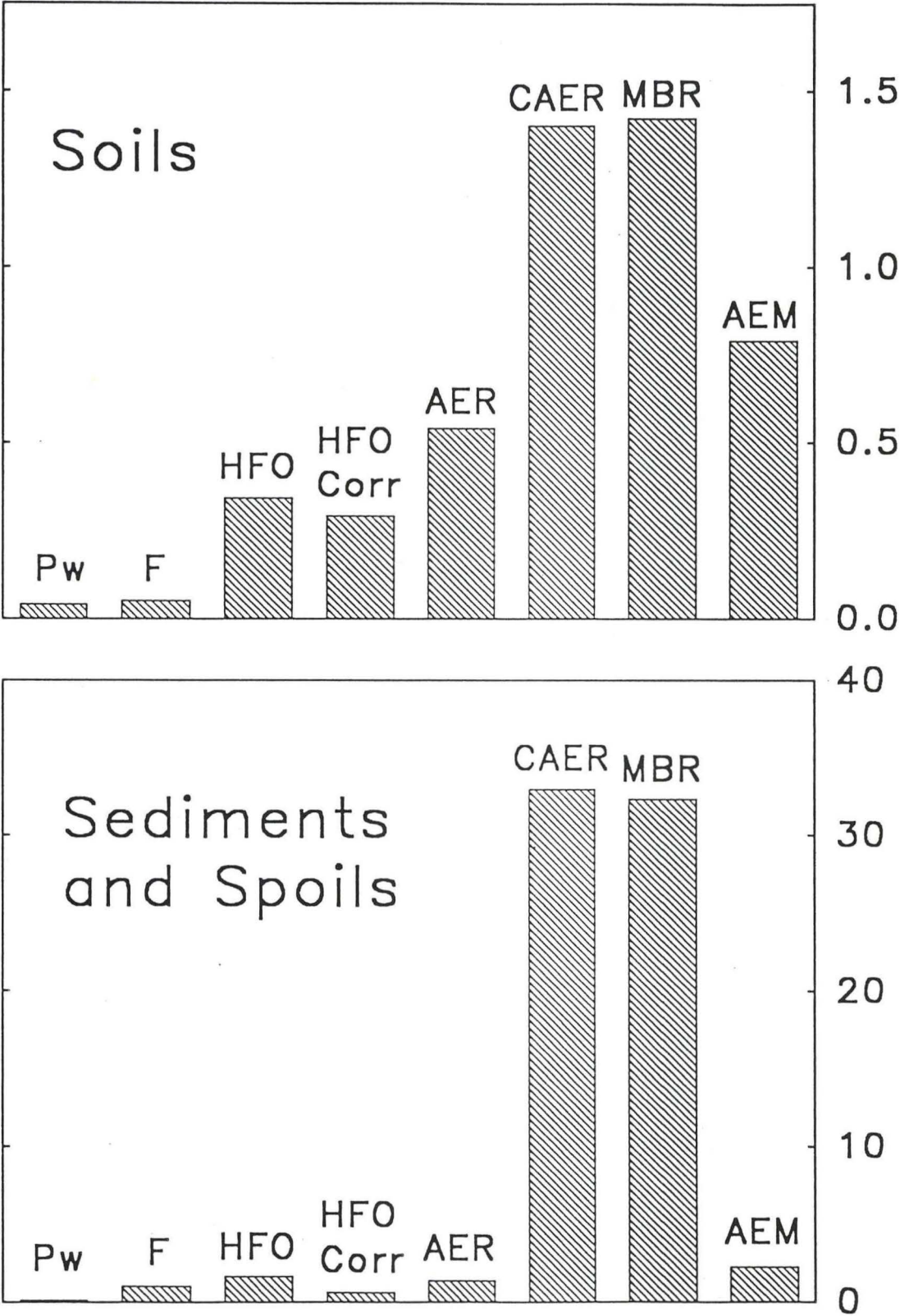
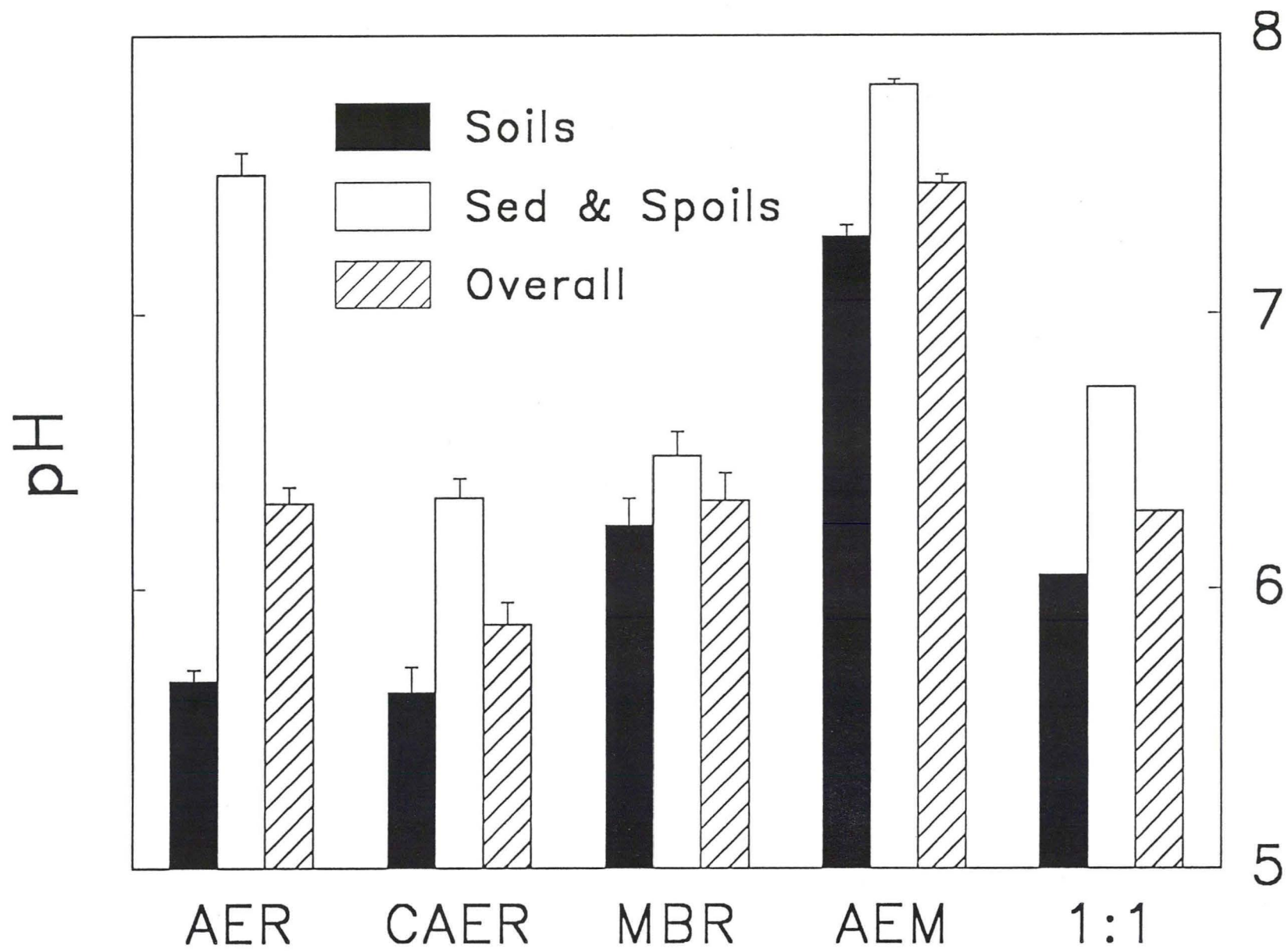


Figure 2



A MODIFIED IRON OXIDE-IMPREGNATED FILTER PAPER TECHNIQUE:

EFFECT OF EMBEDDED PARTICLES

Report 2 of 2

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A MODIFIED IRON OXIDE-IMPREGNATED FILTER PAPER TECHNIQUE:

EFFECT OF EMBEDDED PARTICLES

ABSTRACT

Recently, interest and use of iron oxide-impregnated filter paper, as a sink in soil studies, has increased significantly. Our objective was to investigate the effect of embedded particles in the performance of the modified HFO-impregnated filter paper technique as a sink for multielement release from various P-rich materials. Two phosphate mine spoils, an agricultural soil, and a NBS standard reference material were tested using both a modified HFO-filter paper technique and blank filter paper strips. The effect of different types of filter paper, background electrolyte, solid:solution ratio, Fe extractant, and speed of shaking, on particle retention by the strips was also evaluated. Faster filter paper (larger pores), background electrolyte of lower ionic strength, and higher speed of shaking resulted in larger amounts of embedded particles. Extraction with 0.25 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ + 0.25 M HCl , instead of 0.2 M H_2SO_4 , for 15 min reduced contributions to test values from embedded particles. Extractable-P values for P-rich mine spoils and rock phosphate (NBS standard) were affected significantly by adhering particles, whereas their effect was less pronounced on the agricultural soil (Sterlington). Embedded particles contributed only minor amounts to the extraction of trace metals (Zn and Cd). In order to quantify the effects of adhering particles, it is recommended to include a filter paper blank and to analyze extracts for several elements besides the one of interest.

1 Traditional soil tests often fail to estimate nutrient availability
2 when sparingly soluble sources are present (Saggar et al., 1992). For P,
3 with the current trend toward the use of P fertilizers that are not
4 quickly nor completely soluble, new methodologies and calibrations are
5 being developed to better estimate its bioavailability (Kumar et al.,
6 1991). Perrott et al. (1993) have summarized the performance of
7 traditional soil P tests with phosphate rock (PR) treated soils. Ideally,
8 a soil-P test for PR fertilized soils should reflect residual PR with the
9 potential to dissolve plus adsorbed-P released from soil particles (Saggar
10 et al., 1992). According to Sanyal and De Datta (1991), chemical
11 extractants should (i) not promote PR dissolution during extraction and
12 (ii) extract most of the P or Ca released during dissolution. This has
13 led to a renewed interest in the assessment of availability through batch
14 studies using some type of P- or P + Ca-sinks (Robinson et al., 1992).
15 Ion-exchange resins (e.g., Amer et al., 1955; Sibbesen, 1978), ion-
16 exchange membranes (e.g., Saunders, 1964; Saggar et al., 1990), and more
17 recently Fe-oxide impregnated filter paper (e.g., Van der Zee et al.,
18 1987; Menon et al., 1989b) are sinks commonly used in batch studies.

19 Van der Zee and co-workers (1987) developed a Fe-oxide impregnated
20 technique and successfully described the kinetics of P release of nine
21 closely related, non-calcareous (pH range 4.8 to 5.6), sandy soils from
22 the Netherlands. After 20 h equilibration time, no measurable P remained
23 in solution and led them to conclude that under their experimental
24 conditions, Fe-oxide impregnated paper approximates an *infinite* P sink.
25 Later applications of this technique include parameter assessment in P

kinetics and transport studies (Van der Zee and Van Riemsdijk, 1986; Van der Zee et al., 1986, 1988; Yli-Halla, 1989), and determination of plant available P in soils ranging widely in pH (roughly from 4 to 9) and texture (Menon et al., 1989a, 1989d; Yli-Halla, 1989; Menon et al., 1990a; Chien and Hammond, 1991; Menon et al., 1991b; Ibrikci et al., 1992). Modifications reported in the literature include impregnating the filter paper with both Al and Fe (Menon et al., 1989c; Sharpley, 1991) as well as embedding Fe-impregnated strips in soil (Menon et al., 1990b). Sharpley and co-workers (Sharpley, 1993a, 1993b; Sharpley et al., 1994; Robinson and Sharpley, 1994; Robinson et al., 1994) have successfully used this technique to assess the transport of inorganic and organic phosphorus in agricultural runoff. Previous studies (Buselli and Amacher, 1994a, 1994b) have shown, that under certain conditions, Fe-strips can be potentially used for the quantitative removal of anions and cations from solution.

Ideally, the Fe-strips do not react with the soil and the amount sorbed depends only on the P concentration in solution and not the soil type (Perrott et al., 1993). Preliminary studies and concerns expressed elsewhere (Yli-Halla, 1989) suggest that embedded soil particles may be difficult to remove. Recently, Perrott and Wise (1993), found that adhering soil particles may contribute from 0 to 85% of the phosphorus test value. Small amounts of P-rich particles (e.g., PR, partially acidulated PR, etc.) adhered to the Fe-strips, may subsequently be dissolved in the acid Fe-extraction ($0.2\text{ M H}_2\text{SO}_4$ or $0.25\text{ N NH}_2\text{OH}\cdot\text{HCl} + 0.25\text{ N HCl}$) and significantly affect the results. Nevertheless, there has been an increased use of Fe-impregnated strips in the assessment of P

availability in soils treated with sparingly soluble P-rich amendments (e.g., Chien and Hammond, 1991; Menon et al., 1991a, 1991b; Kumar et al., 1992).

Accordingly, the objective of this study was to investigate the effect of embedded soil particles in the performance of the modified HFO-impregnated filter paper technique as a sink for multielement release from various P-rich materials.

MATERIALS AND METHODS

Samples - Two mine spoils, an agricultural soil, and a NBS Standard reference material were used. The mine spoils were obtained from the cross valley fill at the Maybe Canyon phosphate mine in southeastern Idaho ($42^{\circ}44'$ N $111^{\circ}17'$ W, 2200 m in elevation). The mine is located in the Dry Ridge and belongs to the Phosphoria Formation of the western United States (Van Wazer, 1961). One of the materials consists primarily of a dark-colored chert and the other primarily of black shale (carbonaceous mudstone). Properties of these two materials are shown in Table 1. More detailed information about characterization of the samples can be found elsewhere (Buselli and Amacher, 1994c). The western phosphate rock (see Table 2) was obtained from the National Bureau of Standards (NBS SRM 694), which also came from a phosphate mine in Dry Ridge, Idaho. A Sterlington soil, very fine silty-loam (Typic Hapludalf, coarse-silty, mixed, thermic), collected in Louisiana was used as comparison, since the original method of Van der Zee and co-

workers (1987) was developed for similar non-calcareous soils.

Preparation of HFO-impregnated strips - Preparation of the modified HFO-impregnated strips was done according to the method of Buselli and Amacher (1994a), unless the effects of filter type and of extracting solution on embedded particles was studied.

General - Unless specified otherwise, all experiments were carried out using 1.00 g of air dried material ($< 250 \mu\text{m}$) in 80 ml of solution and shaken in an orbital shaker for 16 h at 150 rpm and $25 \pm 1^\circ\text{C}$. Then, the strips were removed and washed thoroughly, dismounted from the plastic frames, washed again in deionized water and placed in 50-ml plastic centrifuge tubes. Extractions were done in a reciprocating shaker at 180 rpm using 25 ml of $0.25 \text{ N NH}_2\text{OH}\cdot\text{HCl} + 0.25 \text{ N HCl}$ for 15 min. Extracted solutions were analyzed by ICAPES.

Type of Filter Paper and Background Electrolyte - Two types of filter paper, Whatman No. 42 (ashless, slow) and Whatman No. 541 (hardened, ashless, fast), were tested using deionized water, 0.01 M CaCl_2 , and $2.5 \times 10^{-4} \text{ M KCl} + 10 \times 10^{-4} \text{ M MgCl}_2 + 50 \times 10^{-4} \text{ CaCl}_2$ (Baker and Amacher, 1981) as background solutions and two materials (chert and mudstone). Filter paper blanks and iron strips were run in duplicate.

Extractants - Two solutions were tested on their efficiency to remove Fe and the associated sorbed elements from the filter paper, $0.2 \text{ M H}_2\text{SO}_4$ (Van Riemsdijk et al., 1987) and $0.25 \text{ N NH}_2\text{OH}\cdot\text{HCl} + 0.25 \text{ N HCl}$ (Chao and Theobald, 1976). Western phosphate rock (NBS), mudstone, chert, and Sterlington soil were used for these tests. Samples were shaken at 75 and 150 rpm for 16 hr. Duplicate HFO-impregnated strips and blanks were

1 extracted with 25 ml of extracting solution. Due to interference by S in
2 the ICAPES determination of phosphorus, P in H_2SO_4 extracts was determined
3 with a Lachat autoanalyzer using QuikChem method 10-115-01-1-A (revised
4 9/90).

5 Mixing rates - Chert and mudstone spoils, Sterlington soil, and western
6 phosphate rock (NBS) were tested by shaking 1 g of air dried material in
7 80 ml 0.01 M $CaCl_2$ for 0.5, 1, 2, 4, 8 and 16 h at 150 and 300 rpm in an
8 orbital shaker. Preliminary studies showed deterioration of the strips
9 after 32 h and at speeds greater than 300 rpm.

10 Solid:Solution Ratio - The effect of solid:solution ratio was tested with
11 1, 2, and 4 g of mudstone in 80 ml $CaCl_2$. Duplicate HFO-strips and filter
12 paper blanks were shaken for 0.5, 1, 2, 4, 8, and 16 h at 150 rpm.

13 Acid dissolution - Dissolution of embedded particles by 0.25 N $NH_2OH \cdot HCl$
14 + 0.25 N HCl was estimated by extracting 0.100, 0.050, and 0.025 g of each
15 material with 25 ml of solution for 15 min in a reciprocating shaker at
16 180 rpm.

17 18 RESULTS 19

20 Amounts of Ca and P recovered from blank filter paper are shown in
21 Figure 1. Statistically (three-way analysis of variance), mudstone
22 adhered to the filter paper significantly more ($P < 0.001$) than chert as
23 inferred from values of both Ca and P recovered. Whatman No. 541 filter
24 paper trapped significantly more particles ($P < 0.001$), regardless of
25 background electrolyte or type of material, than Whatman No. 42. As

expected, particles adhered more easily to the faster (larger pores) filter paper. Using the Student-Neuman-Keuls test for multiple comparisons (Einot and Gabriel, 1975), suspending the material in 0.01 M CaCl_2 resulted in significantly ($P < 0.05$) less embedded particles than either deionized water or Baker's solution.

The effect of different extractants on removal of Fe and associated sorbed species from the strips plus dissolution of material embedded in both HFO strips and filter paper blanks for western PR (NBS) is shown in Figure 2. There was a significant ($P < 0.001$) difference in the amounts extracted from both blanks and HFO-strips between suspensions shaken at 75 and 150 rpm. Invariably, the standard errors (SE) between replicate measurements obtained with hydroxylamine hydrochloride were lower than the ones obtained with sulfuric acid. Sulfuric acid extraction of blank strips shaken at 150 rpm yielded higher values than when extracted with 0.25 N $\text{NH}_2\text{OH}\cdot\text{HCl}$ + 0.25 N HCl , suggesting higher dissolution of embedded particles. Regardless of speed of shaking, hydroxylamine extractions yielded highly significant ($P < 0.001$) differences between blank and HFO-strips for all elements (Fig. 2). On the other hand, there were no significant differences ($P < 0.05$) between blanks and HFO-strips for Ca and P with H_2SO_4 as extractant. Similar results were obtained with the other materials.

Figure 3 shows the molar ratio of P:Ca obtained from extractions of both blank filter paper and HFO-strips. The ratios P:Ca of the blanks closely follow dissolution of the materials with $\text{NH}_2\text{OH}\cdot\text{HCl}$ + HCl , furthermore, the values obtained from the NBS certificate of analysis

correspond closely with the PR extracted values. In the case of HFO-strips, suspension pH affects the P:Ca ratios. Ratios for the HFO-strips will include dissolved species adsorbed by the strip plus dissolution of embedded material. As reported elsewhere (Buselli and Amacher, 1994a; 1994b), sorption of calcium from solution becomes significant at pH values higher than 6, while P sorption decreases markedly from pH 6.5 to pH 8. With mudstone and western PR, the slightly lower P:Ca ratios obtained with strips as compared to blanks could be attributed to significant levels of dissolved calcium removed from solution. As suspension pH decreases (see chert and Sterlington soil, Fig. 3), the HFO-strips yielded narrower P:Ca ratios than filter paper blanks.

In the case of trace metals, contributions to test values by adhering particles are less significant (see Figs. 4 and 5). Since total content of trace metals in embedded particles is very low (see Table 2), adsorption of dissolved metals by the HFO-strip is the dominant mechanism of metal removal from suspension. Ratios of Zn:Ca and Cd:Ca in the blank filter paper correspond closely to the values obtained by hydroxylamine hydrochloride/hydrochloric acid as well as the NBS values (for PR). Ratios for trace metal:Ca are much narrower for the HFO-strips, and suggest that a blank baseline correction could yield actual dissolved metal removal.

The Cd:Ca ratios in Fig. 5 show that the amount of particles embedded per strip is not affected significantly by the solid:solution ratio of the suspension. For example, the total amounts of Ca extracted from blank strips removed from suspension after 8 h shaking at 150 rpm

were 4.9 μmol at a solid:solution ratio of 1:80, 5.7 μmol at 1:40 and 6.2 μmol at 1:20. Although there is a slight increase with increasing amounts of solid in the suspension, the data suggest that the filter paper would retain a finite maximum amount of fine particles per unit area regardless of total amount of solid in suspension.

DISCUSSION

As reported by Perrott and Wise (1993), the effect of particles embedded in the filter paper may contribute significantly to the P test values obtained with HFO-strips. Although sonication removed from 55 to 72 % of the adhering soil, they found that it also removed P adsorbed by the HFO-strips from synthetic solutions. Our results indicate that a reduction in the amounts of particles adhering to both the HFO-strips and blanks can be obtained by using different types of filter paper. Further exploration into the use of different papers as well as other materials may yield a removable solid phase that does not trap suspended particles. For example, cation exchange resin-affixed hydroxy-aluminum has been used as a sink for orthophosphate (e.g., Hsu and Rich, 1960; Hsu and Rennie, 1962). Later, Huettl and co-workers (1979) developed a technique, using hydroxy-Al resin, that successfully predicted algal-available P in runoff suspensions (see also Mueller et al., 1984; Andraski et al., 1985; Dorich et al., 1985). Applications of recent developments in the preparation of thin oxide films (e.g., Orel et al., 1994) as well as use of new durable resin membranes as supporting materials for oxides (e.g., Cooperband and

Logan, 1994) should be studied.

Shaking speeds affect significantly the amounts of particles adhered to the filter paper. Doubling the speed from 75 to 150 rpm resulted in at least a two-fold increase in the amounts removed from suspension by both blanks and HFO-strips (Fig. 2). On the other hand, increasing shaking speeds to 300 rpm resulted in the deterioration on both blanks and strips (visible around edges) due to particle abrasion. Therefore, shaking speeds should be chosen high enough so as to insure complete suspension of solids in solution while preventing excessive abrasion by suspended particles.

With materials adhering to the HFO-strips, the type of extractant and time of extraction should be carefully chosen to minimize contributions from embedded particles. Extraction procedures reported to remove Fe from the strips are: 40 ml of 0.1 M H_2SO_4 for 1 h (Menon et al., 1989b), 40 ml of 0.2 M H_2SO_4 for 1 h (Yli-Halla, 1989), for 4 h (Van der Zee et al., 1987), 0.5 M H_2SO_4 (Perrott and Wise, 1993), and 40 ml of 0.5 M NaOH for 1 h (Robinson and Sharpley, 1994). In theory, as long as all the Fe is dissolved, all methodologies should yield comparable results. But, in the presence of adhering particles the procedures will extract different amounts and forms of P present in such particles. Extraction times longer than the ones needed for Fe removal from the filter paper should be avoided. We found that using 25 ml of 0.25 N $\text{NH}_2\text{OH}\cdot\text{HCl}$ + 0.25 N HCl and shaking for 15 min at 180 rpm removes over 99 % of the Fe in freshly precipitated HFO-strips (Buselli and Amacher, 1994a). Smaller standard errors and lower extraction values for filter paper blanks favor

the use of hydroxylamine hydrochloride/hydrochloric acid over 0.2 M H₂SO₄ (Fig. 2).

The pH of the suspensions should be monitored since adsorption onto iron oxides is highly pH-dependent. Furthermore, with acid soils like the ones used by Van der Zee et al. (1987) and Kuo and Jellum (1994), not only will the suspension pH values be probably optimum for P adsorption, but presence of Ca in the extracts may indicate the presence of embedded particles. We recommend, under all conditions, the use of blank filter paper strips to quantify the contribution from adhering particles.

Under the current methodologies, the use of HFO-strips as sinks for element release from soils, sediments, and soil components should be used with caution. According to Perrott and Wise (1993), even though the extracted P values (adsorbed + adhered) may reflect the ability of the soil to supply phytoavailable P, it can not be assumed that the HFO-strips measure only desorbed P. With sandy soils, or when determining desorption of elements present in trace amounts (e.g., heavy metals), contributions, if any, due to embedded particles could be corrected in order to obtain desorption values. On the other hand, when studying soils with large amounts of colloidal particles or with particles rich in the element of interest, effects are significant and corrections may prove unreliable.

CONCLUSIONS

Under certain conditions, particles embedded in HFO-strips may have a significant effect on the extraction values obtained by the technique.

Although good correlations have been reported between phytoavailable P obtained with the technique and with standard available P methods, as well as with plant uptake, it can not be assumed *a priori* that the HFO-strips extract only desorbed P. The quantity of adhering particles will depend on:

1. Type of solid sample (soils, sediments, soil components, etc.). Colloidal material will tend to adhere more easily than coarser particles.
2. Type of filter paper. Faster (larger pores) filter papers will trap more particles than slower filters.
3. Ionic strength. Lower ionic strengths (i.e., more disperse system) result in larger amounts adhering to the HFO-strips.
4. Speed of shaking. Increasing speeds will allow more particles to penetrate through fibers in the paper resulting in more particles being trapped.

The composition and reactivity of the embedded particles is more important than total amounts collected by the strips. Therefore, the type of extractant used to remove Fe from the filter paper and the conditions of extraction (time, shaking speed, etc.) may have a significant effect on the values obtained.

In its current form, the applicability of the technique to measure desorption of various elements is limited by the type of materials used and by suspension pH. On the other hand, the technique has proven extremely valuable in the study of sorption processes from solution onto hydrous oxides (Buselli and Amacher, 1994a; 1994b). It is recommended in

future studies with soils, soil materials, and natural waters to: (i)
include blank filter paper to quantify the effects of adhering particles,
if any, (ii) monitor suspension pH, and (iii) obtain analyses of the
extracted solution as complete as possible to gain a better understanding
of any other processes that may be occurring.

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25

Table 1. Selected physical and chemical characteristics of mine spoils from the Maybe Canyon Mine, Idaho

| | Mudstone | Chert | Reference |
|---|----------|-------|--|
| pH | 7.5 | 6.3 | McLean (1982) |
| TOC ^a (%) | 5.25 | 0.76 | Nelson & Sommers (1982) |
| ECEC ^b (cmol _c /kg) | 24.77 | 3.76 | 1 M NH ₄ NO ₃ , unbuffered |
| MnO ₂ (%) | 0.031 | 0.125 | Chao (1972) |
| Amor. Fe (%) | 0.649 | 0.112 | Chao & Zhou (1983) |
| Crys. Fe (%) | 1.103 | 0.657 | Shuman (1982) |
| Dolomite (%) | 0.15 | 0.00 | Holtzclaw et al. (1986) |
| Calcite (%) | 0.36 | 0.08 | " |
| Sand (%) | 37.5 | 66.9 | Gee & Bauder, (1986) |
| Silt (%) | 43.5 | 23.4 | " |
| Clay (%) | 19.0 | 9.7 | " |

^a TOC - Total organic carbon

^b ECEC - Effective cation exchange capacity

Table 2. Western Phosphate Rock: Standard Reference Material 694, National Bureau of Standards (data from Certificate of Analysis).

| Element | mmol/kg of PR | Element | mmol/kg of PR |
|---------|---------------|-----------------|---------------|
| Al | 353 | Mn | 1.6 |
| Ca | 7775 | Na | 277.5 |
| Cd | 1.2 | P | 4255 |
| Fe | 98.9 | Si | 1864 |
| Mg | 81.9 | Zn [†] | 23.3 |

[†] Non-certified

FIGURES

- Figure 1. Effect of type of filter paper and background electrolyte on the amounts of Ca and P extracted by blank filter papers. Water: deionized water, Baker's: , and CaCl_2 : 0.01 M CaCl_2
- Figure 2. Effect of different shaking speeds (75 and 150 rpm) and extracting solutions (H_2SO_4 : 0.2 M H_2SO_4 , and $\text{NH}_2\text{OH} \cdot \text{HCl}$: 0.25 N $\text{NH}_2\text{OH} \cdot \text{HCl}$ + 0.25 N HCl) on extraction values for western phosphate rock.
- Figure 3. Molar P:Ca ratios extracted by the HFO-strips for the 4 different materials. Speed of shaking: 150 rpm, extractant: 0.25 N $\text{NH}_2\text{OH} \cdot \text{HCl}$ + 0.25 N HCl , solid:solution ratio: 1:80. Dotted line represent calculated values for PR from the NBS Certificate of Analysis, dashed lines are values obtained from direct extraction of materials with 0.25 N $\text{NH}_2\text{OH} \cdot \text{HCl}$ + 0.25 N HCl .
- Figure 4. Molar Zn:Ca ratios extracted by the HFO-strips for the different materials (no measurable amounts of zinc were obtained with the Sterlington soil). Speed of shaking: 150 rpm, extractant: 0.25 N $\text{NH}_2\text{OH} \cdot \text{HCl}$ + 0.25 N HCl , solid:solution ratio: 1:80, except when noted. Dotted line represent calculated values for PR from the NBS Certificate of Analysis, dashed lines are values obtained from direct extraction of materials with 0.25 N $\text{NH}_2\text{OH} \cdot \text{HCl}$ + 0.25 N HCl .
- Figure 5. Molar Cd:Ca ratios extracted by the HFO-strips for phosphate rock and mudstone (no measurable amounts of cadmium were obtained with chert or the Sterlington soil). Speed of shaking: 150 rpm, extractant: 0.25 N $\text{NH}_2\text{OH} \cdot \text{HCl}$ + 0.25 N HCl , solid:solution ratio: 1:80, except when noted. Dotted line represent calculated values

for PR from the NBS Certificate of Analysis, dashed lines are values obtained from direct extraction of materials with 0.25 N $\text{NH}_2\text{OH}\cdot\text{HCl}$ + 0.25 N HCl.

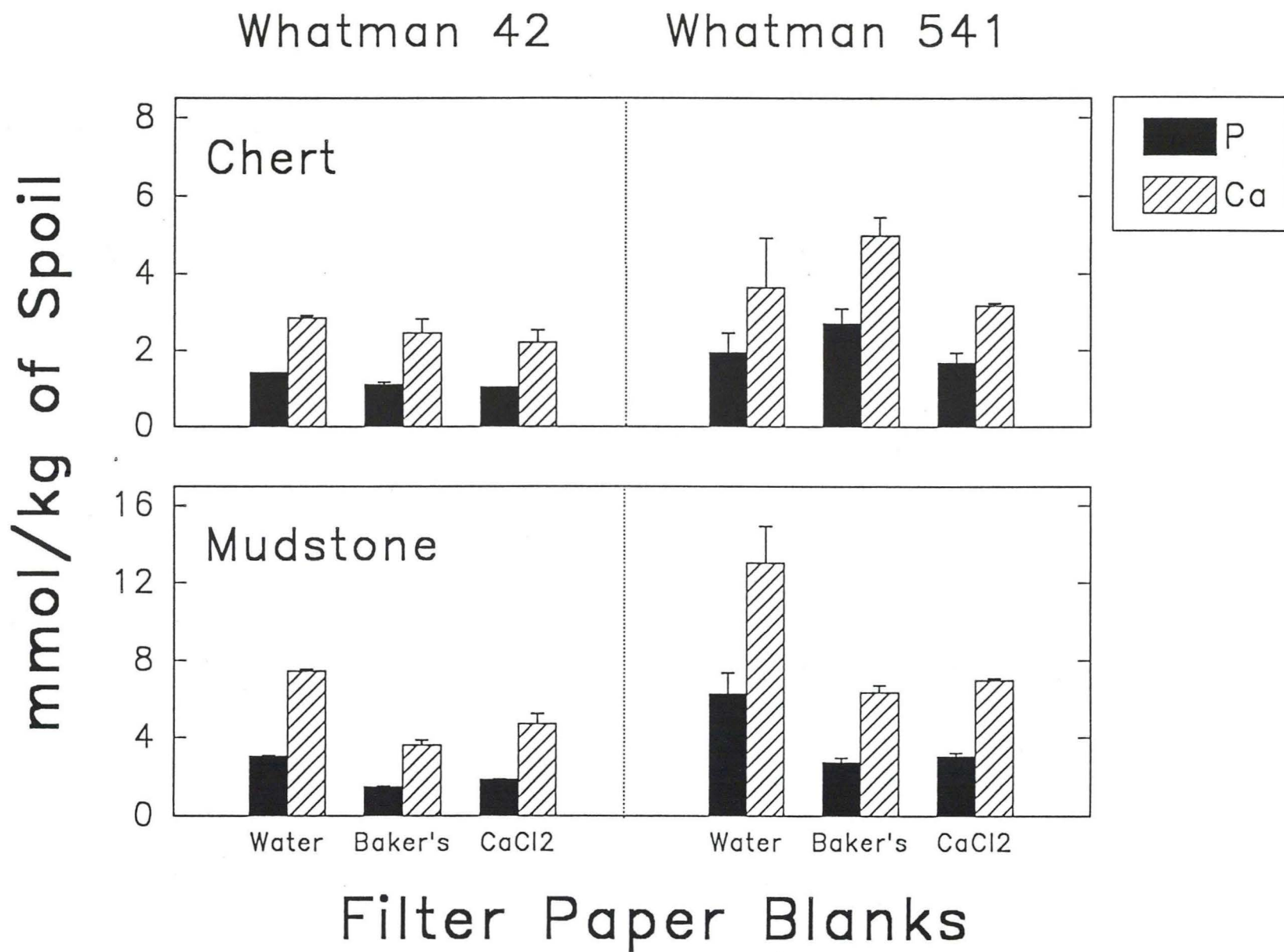


Figure 1

Figure 2

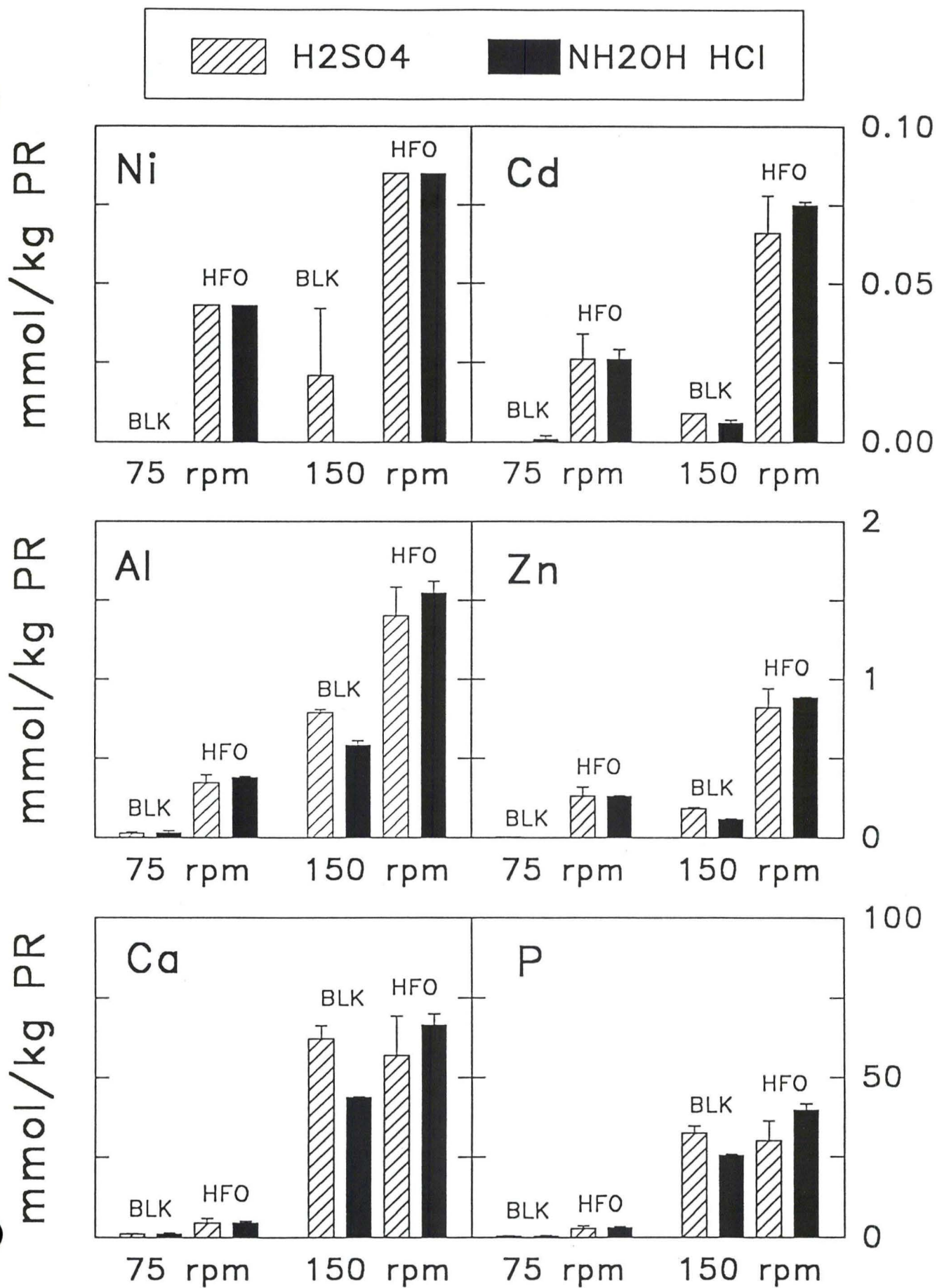


Figure 3

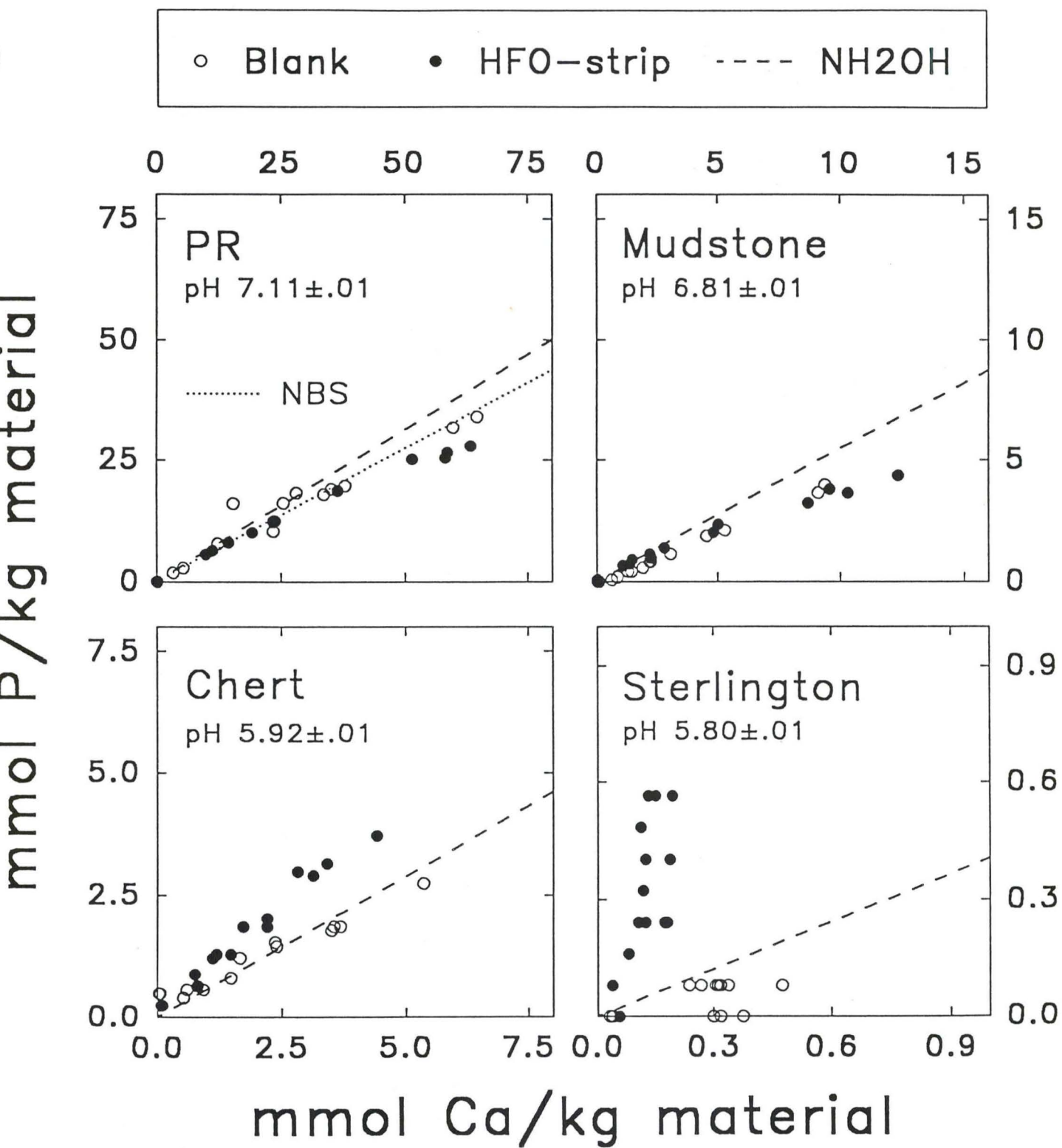


Figure 4

mmol Zn/kg material

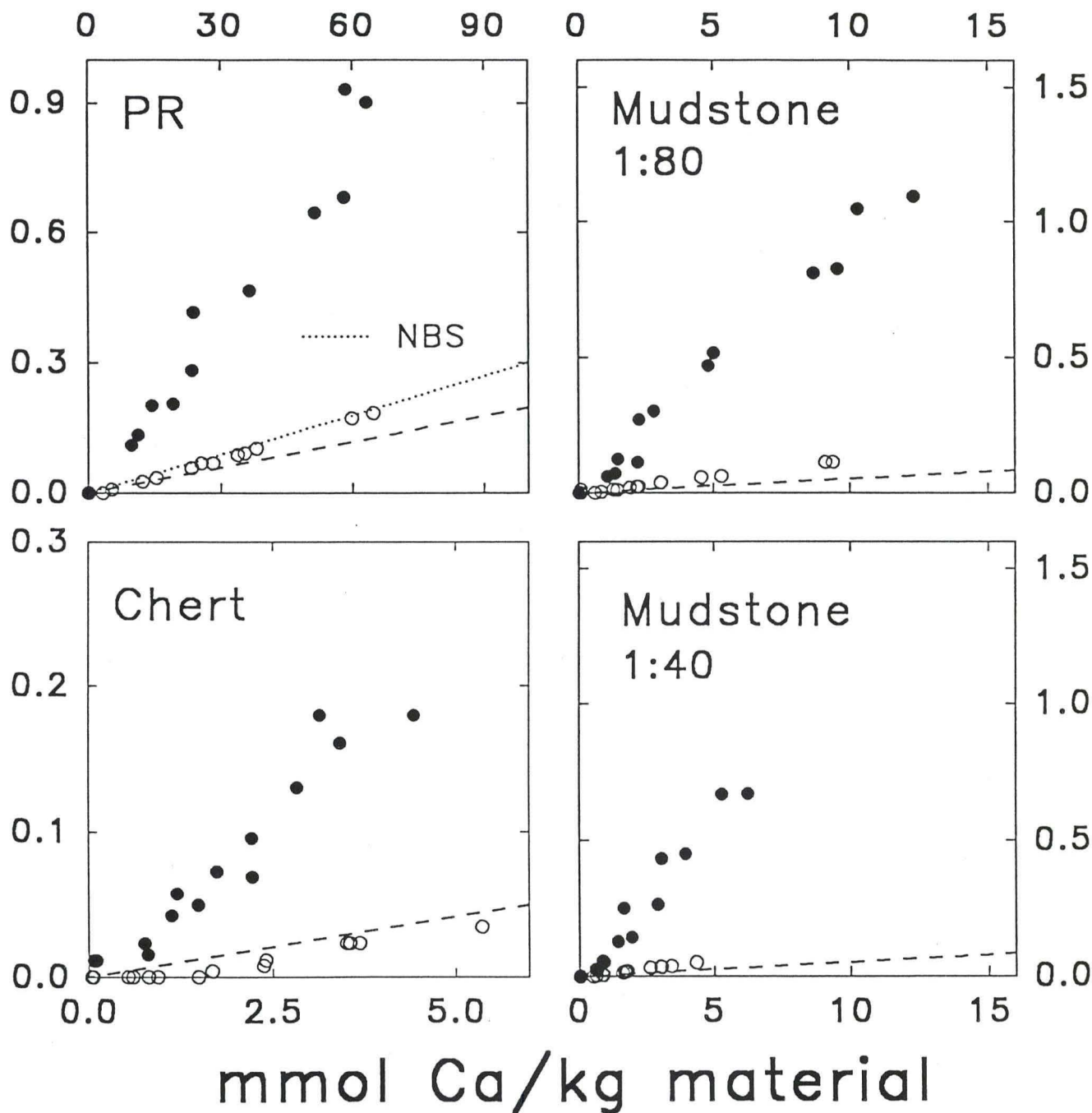
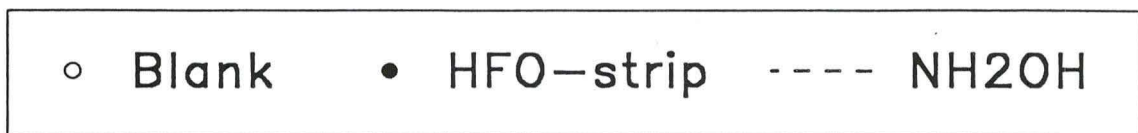


Figure 5

